

**PHOTOACOUSTIC ANALYSIS OF THE EVOLUTION FROM SOLS TO AGED GELS. COMPARISON OF DIFFERENT INITIAL TITANIA SOLS<sup>1</sup>**

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## ABSTRACT

We propose the use of correlation analysis of the photoacoustic signal changes during the sol-gel-aging evolution of titania sols prepared from the hydrolysis of titanium n-butoxide in alcoholic, aqueous, and micellar medium which provide different initial conditions and different evolution pathways. The photoacoustic experiments were done either at constant temperature for monitoring the initial evolution of the system, or under heating at 2°C for monitoring molecular processes related to drying, sintering and crystallization. Results obtained from photoacoustic measurements display higher sensibility when compared with those from Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). The evolution of these systems show instabilities below and above gelation, as well as during thermal treatment. These stabilities are minimized when the thermal treatment is performed on gels aged several months, and can be associated to molecular rearrangements or oscillating chemical reactions. For all the systems studied, the sensitivity of the correlation analysis recovered from photoacoustic signals allows to detect a transition in the 100-150°C range.

**KEY WORDS:** correlation analysis, oscillating reactions, phase transition, photoacoustic, sol-gel, TiO<sub>2</sub>.

## 1. INTRODUCTION

In recent years, the new low-temperature pathway for the synthesis of glasses and ceramics known as Sol-Gel (SG) has been of great interest for science and technology. The sol-gel process is based on the hydrolysis of suitable molecular precursors and condensation of oligomers, thus the control of relative reaction rates allow to obtain tailored materials that are more homogeneous than those obtained through conventional high temperature processes. The precursor participates in hydrolysis and condensation reactions that forms particles (*particulate sol*) or polymers (*polymeric sol*), uniformly distributed in the bulk solvent [1, 2]. The particle-particle and particle-solvent interactions among these units lead to an increase in the viscosity of the solution until a *gel* is formed [3]. To obtain a material with specific characteristics, one must control the hydrolysis and condensation reactions, since these two compete to determine the nature of the final products.

The sol-gel evolution has great influence in the porous structure of the final material, usually obtained after the application of a thermal program. The simplest picture of gelation is that clusters grow by condensation of polymers or aggregation of particles until the clusters collide; then links form between the clusters to produce a giant cluster that is called a gel. In this process no latent heat is evolved, but the viscosity rises abruptly and elastic response to stress appears [1]. The sudden change in rheological behavior is usually used to identify the *time of gelation*,  $t_g$ . The SG transition is therefore the one that implies a critical evolution of the mechanical properties of the material. The structural changes and the dynamic properties at microscopic and macroscopic levels below and above  $t_g$  has been studied by many techniques [1, 4, 5, 6, 7, 8, 9, 10, 11]. In particular, acoustic waves generated either by an appropriate oscillator [12], or by impinging light onto an absorber

(usually carbon films) close to the material under study [4] ,or by chromophores included in the system has been explored [11, 13, 14] for the study of sol to gel evolution of silica and titania based systems.

The photoacoustic technique has proven to give clear evidence of processes occurring at times well before and well after the gelation time, periods for which other techniques show little signal variations. However, the recovering of information from the evolution of photoacoustic waves requires a mathematical analysis of the whole signal and not only from the amplitude and time of the first acoustic wave. In a previous work, a new approach based in the correlation analysis of the photoacoustic signal changes allows to determine a phase transition in BaTiO<sub>3</sub> ceramics [15]. This result impulse us to apply the same strategy in order to determine the stability and transitions in titania based systems obtained from different initial sols.

The photoacoustic signal (PA) depends on several factors. In the direct coupling method, the acoustic wave is related to the thermal expansion  $\Delta V_{th}$  of the irradiated volume  $V_o$ . This expansion creates a pressure wave, which travels outwards at the velocity of sound, and the electrical signal generated in the transducer is proportional to pressure [16]. The interaction between the laser beam and the system produces a photoacoustic signal say PA(t, X<sub>i</sub>) where i indicates the size of the temporal signal, and X<sub>i</sub> is a parameter to be considered in each experiment [17, 18]. In our case, X<sub>i</sub> is the time for the sol to aged gel evolution, or X<sub>i</sub> is the temperature for thermal processing experiments. Once the functions are obtained they can be mathematically manipulated to extract the important physical information as the temporal profile of the acoustic pressure depends on the spatial properties and microscopic characteristics of the interaction regions. Therefore, this kind of experiments should be able to detect fundamental structural changes in the material as a consequence of the interaction between a pulsed laser beam and the sample.

In this work, we use the photoacoustic method to follow the thermoelastic changes that occur during the sol-gel evolution, as well as that of the material obtained after specific thermal processing on the basis of correlation between acoustic signals. The analysis performed involves two types of correlation, the first one over successive functions PA(t, X<sub>i</sub>) and PA(t, X<sub>i+1</sub>), which will reveal those changes occurring in the specimen in the interval (X<sub>i+1</sub>-X<sub>i</sub>). The correlation, R, between PA(t, X<sub>i</sub>) and PA(t, X<sub>i+1</sub>) will be R= 1 if PA(t, X<sub>i</sub>) and PA(t, X<sub>i+1</sub>) are identical functions, but R<1 if any change occurs in the interval (X<sub>i+1</sub>-X<sub>i</sub>). This correlation is very sensitive to local changes in the material, and produces a X dependent curve which exhibits noticeable resolution characteristics, analysis that we will denote as stability [17]. With the second correlation, a comparison is carried out between PA(t, X<sub>1</sub>) and every PA(t, X<sub>i</sub>) function, where i=1, 2, 3, ..., as performed in any standard correlation [19]. Therefore, the appropriate conclusions can be reached by the analysis of the X dependence of one or both correlation types between events.

The sol-gel system selected for these studies is based on the hydrolysis of titanium n-butoxide in alcoholic, aqueous, and micellar medium which provide different initial conditions that should lead to different evolution pathways. From our previous studies, the alcoholic system prepared in buthanol can be considered as polymeric, and gives transparent gels in few minutes [11]. For the hydrogel the solvent is water, and the gel network is formed by interaction between partially hydroxylated particles [14]. Finally, gels

obtained from water confined in AOT reverse micelles [20, 21] give an example of a gel produced by interaction of particles in a solvent with low vapour pressure, such as isooctane. Results obtained from photoacoustic experiments are compared to those obtained from replicate samples by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). In this way, the processes that occur from the sol can be evaluated, especially the stability of the system as the solvent diffuses and evaporates, and links between units are formed.

## 2. PREPARATION OF THE SAMPLES

In this work, all synthesis of TiO<sub>2</sub> sol-gels were based on the hydrolysis of titanium n-butoxide (Ti(OBu<sup>n</sup>)<sub>4</sub>, Fluka Chemika). This alkoxide is a good precursor for TiO<sub>2</sub> as it does not react very fast with water. This is because of the O-Bu group, with 4 carbon atoms, is sufficiently large, but does not avoid oligomerization. The polymerization of Ti(OBu<sup>n</sup>)<sub>4</sub> dissolved in 1-butanol or in water (alcoholic or aqueous media) is controlled kinetically with an inhibiting acid (HCl) that avoids the precipitation of the oxide or the formation of large heterogeneous zones. In micellar media, precipitation is avoided by constrained water within AOT reverse micelles. The hydrolysis of the molecular precursor, Ti(OBu<sup>n</sup>)<sub>4</sub>, produces a gel composed by a porous interconnected matrix, formed by linked oxo-polymers with very stable Ti-O-Ti bridges that contain solvent, non reactant precursors and oligomers.

### 2.1. Alcoholic media

The samples were prepared according to the method described by Puccetti and Leblanc [4] that is a modification of that proposed by Sanchez and coworkers [22]. A mixture of 0.1 mL of 1 M HCl (J.T.Baker, 36.5-38.0%) and 1.2 mL of 1-butanol (J.T.Baker, 99.90%) was agitated for 15 minutes at room temperature. Then, at a time referred  $t_0$ , 0.8 g of Ti(OBu<sup>n</sup>)<sub>4</sub>, was added dropwise, maintaining agitation until complete homogenization of the sample in 40–60 s.

### 2.2. Micellar media

The micellar solution was prepared by dissolving AOT (SigmaUltra, minimum 99%) in isooctane (Fermont, HPLC/spectrophotometric grade, 99.8%) with further addition of water up to a fixed H<sub>2</sub>O/AOT molar ratio ( $w_0 = 10$ ). Ti(OBu<sup>n</sup>)<sub>4</sub> dissolved in isooctane was further added to the micellar system.

### 2.3. Hydrogels.

Titania sols were obtained by hydrolysis of Ti(OBu<sup>n</sup>)<sub>4</sub> in 3.2 M HNO<sub>3</sub> (J.T.Baker, analytic grade) under stirring at 25 °C. The water: alkoxide mole ratio was 185:1. The sol was further dialyzed against water until pH ~ 3.5 using dialysis membranes (Medicell International Ltd; Size 9 Inf Dia 36/32"-28.6 mm:30M). The gels were stored at 4 °C. All reagents were used without further purification, and water was tridistilled.

### 3. EXPERIMENTAL SETUP

The photoacoustic experimental setup employed consisted of [15, 17]: a) a pulsed Nd:YAG laser (10 Hz, 5 ns pulse width); b) a beam splitter and a pyroelectric detector with display for real time monitoring of the energy variations of the laser ( $< 200\mu\text{J}$ ); c) a cylindrical PZT transducer, having a resonance frequency at 240 kHz. The signals without amplification were recorded in a digital oscilloscope and sent to a PC through a GPIB interface. Heating experiments were carried out in normal laboratory condition from 20 to 300 °C, using a well-controlled electrical tubular furnace. The analyzed measurements are the results of averaging at least 300 photoacoustic signals for a given temperature or time. Photoacoustic measurements are performed in a dry air atmosphere with a heating temperature rate of 2 °C/ min.

DTA and TGA measurement (atmosphere: air) were carried out in the same conditions of photoacoustic experiments with a Differential Thermal Analyzer DTA-50 Shimadzu and Thermogravimetric Analyzer TGA-51 Shimadzu systems, respectively.

### 4. RESULTS AND DISCUSSION

#### 4.1. Sol-gel transition

Figure 1.a shows the evolution of standard correlation analysis obtained from the PA signal as the titania based system evolves from the initial sol. The first point ( $t=0$ ) corresponds to the mixture of reagents at 60°C. This temperature was chosen in order to get a gel for the titania based aqueous system (hydrogel). The time elapsed between the mixture of reagents and the collection of the first point is ca. 1 min, enough to guarantee that the sample has reached the oven temperature. Each curve in the figure is representative of a different precursor sol. In all cases there is a marked decrease at the beginning of the experiment followed by oscillations that are more pronounced in the most particulate system, i.e. the hydrogel. The stability analysis shows a more clear sketch of the system behavior, as depicted in figure 1.b. For the alcoholgel, the first minimum at ca. 8 min coincides with the visual inspection of  $t_g$ . On the other hand, the hydrogel, a particulate sol with lower gelation kinetics [14], is characterized by a high instabilities up to 50 min. The micellar system, with low water contents, exhibit an intermediate behavior with instabilities up to 35 min. Although, as discussed below, evaporation of the solvent and gelation occur simultaneously the peak discriminated in the stability plots at 40 min for the hydrogel can be associated to the sol-gel transition previously determined by viscosity measurements [14]. For the micellar system, it is hard to distinguish if the sol-gel transition takes place at 12 min or at 20 min as  $t_g$  for these systems is strongly dependent on the hydration of AOT employed for preparing the micellar solution [20].

TGA experiments with replicate systems show that 80% of weight is loss in the first 20 min for the alcoholgel, 60% in 10 min for the micellar system, and 100 % in 50 min for the hydrogel. These mass losses shown in figure 2 correspond to the evaporation of the solvent, butanol in the case of alcoholgel, isooctane in the case of micellar system, and water for the hydrogel. These results support the idea that instabilities are not directly related to the evaporation of solvent. Therefore, instabilities represent changes in the thermoelastic of gels that might be associated to molecular rearrangements producing changes in the

secondary structure of the gel, to the reversibility of Ti–O–Ti bonds, to branching and crosslinking reactions, or to oscillating chemical reactions. To our knowledge, there are few reports on instabilities of gels even one should expect it occurrence in complex systems. Kaufman and Avnir [23] found instabilities above  $t_g$  in silica sol-gel-xerogel systems from fluorescence measurements of a sensitive probe (pyrene) included in the evolving system. Guizard et al [24] also detect oscillations in the emission of either pyrene or lanthanide ions during the evolution of silica and titania based gels synthesized in micellar solutions.

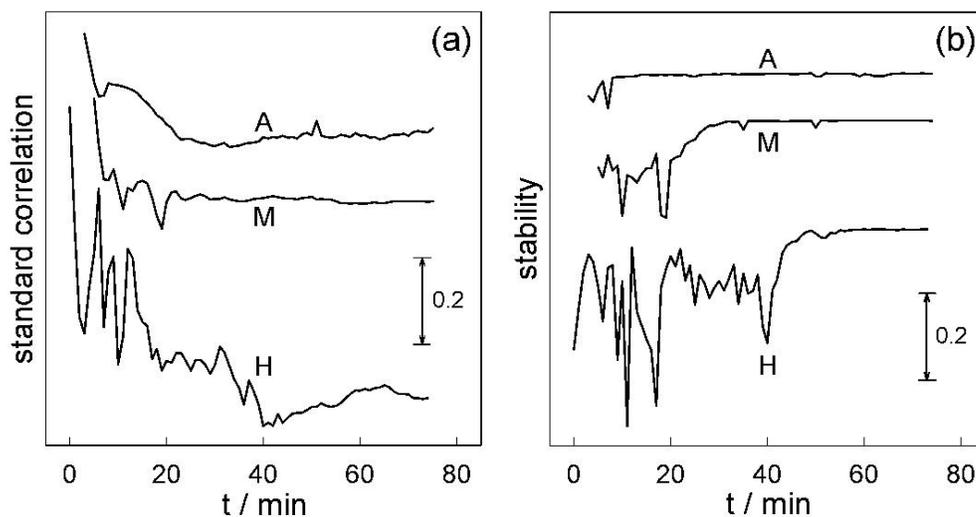


Figure 1. Standard correlation (a) and stability analysis (b) of photoacoustic signals as a function of time for different TiO<sub>2</sub> systems: alcoholgel (A), hydrogel (H) and micellar gel (M).

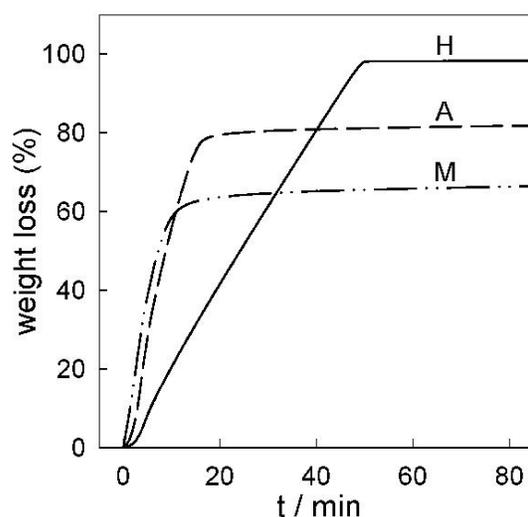


Figure 2. Weight loss obtained by TGA as a function of time for different TiO<sub>2</sub> systems: alcoholgel (A), hydrogel (H) and micellar gel (M).

## 254.2. Thermal evolution of gels.

As shown in figures 1 and 2, at 80 min a high fraction of the solvent is evaporated, and all systems exhibit a stable behavior. At this point, the temperature is raised at  $2^{\circ}\text{C min}^{-1}$  in order to promote drying, sintering and crystallization, as well as combustion of any organic. Figure 3 shows the standard correlation and stability analysis of the photoacoustic signals as a function of temperature, and figure 4 shows the corresponding TGA results obtained with replicate samples. These experiments confirm that the instabilities recovered from the PA signal are not related to changes in the mass of the sample, and is a characteristic of gels that can be only detected by sensitive techniques. Thus, these instabilities can be unambiguously associated to changes in the molecular level, as proposed above. It is important to stress that previous works reporting instabilities are based on experiments sensitive to local environments, whereas the correlation analysis of PA signal gives information on the behavior of the whole system. Although the origin of molecular rearrangements giving oscillatory changes in thermoelasticity cannot be directly obtained from PA results, it is possible to stress that they are more evident in the most particulated systems, such as hydrogels and micellar systems, and become negligible for the most polymeric gels. Following the rationale of Kaufman and Avnir [23] these instabilities can be tentatively associated to oscillating reactions of chaotic nature. Another possible origin of these instabilities might be chemical reactions leading branching of chains or to cross-linking between chains.

The stability function (figure 3.b) shows a clear peak located at  $120^{\circ}\text{C}$  for the alcoholgel,  $110^{\circ}\text{C}$  for the micellar system, and  $100^{\circ}\text{C}$  for the hydrogel. At these temperatures there are no special features in the TGA plots of figure 4, nor in the differential thermal analysis (DTA) plots shown in figure 5. DTA experiments reveal an exothermic process for the alcoholgel and for the micellar system at  $215^{\circ}\text{C}$  and  $236^{\circ}\text{C}$ , respectively. These processes are related to the small weight loss found for these samples in TGA plots that are assigned to the decomposition of organic matter present in these samples. Thus, the peaks discriminated in figure 3.b represent a singular point in the gel evolution due to particular molecular rearrangements. This singularity is the main feature recorded in the thermal evolution of gels aged 4 months in a capped seal, as shown in figure 6.

The fact that long term aged gels do not exhibit instabilities upon thermal treatment, but display a clear peak at  $130$  and  $140^{\circ}\text{C}$ , respectively (see figure 6), allow us to affirm that between  $100$  and  $140^{\circ}\text{C}$  there is a structural transition that is intrinsic of titania based gels. This transition is not accompanied by heat evolution, and can be tentatively assigned to a particular molecular rearrangement. For aged gels, this transition is clearly seen both in stability and standard correlation plots, whereas for fresh gels the instabilities of the system mask the corresponding peak that is clearly distinguished from the stability function.

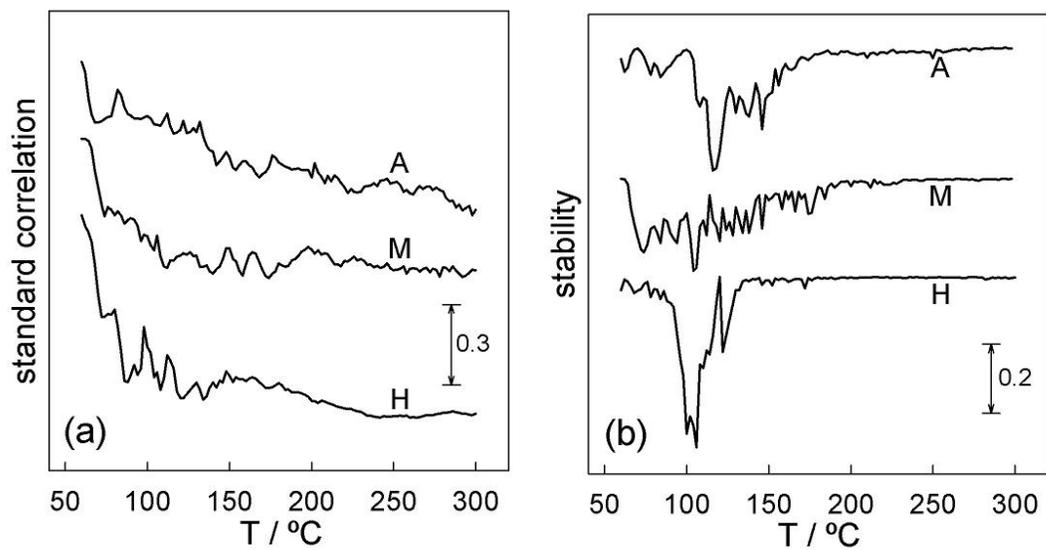


Figure 3. Standard correlation (a) and stability analysis (b) of photoacoustic signals as a function of temperature for different  $\text{TiO}_2$  systems: alcohol gel (A), hydrogel (H) and micellar gel (M).

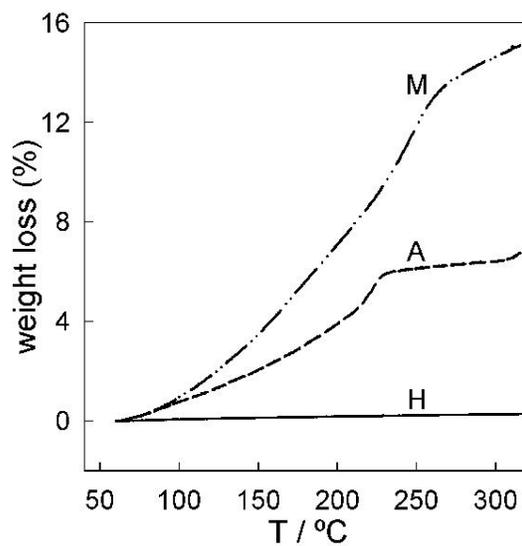


Figure 4. Weight loss obtained by TGA as a function of temperature for different  $\text{TiO}_2$  systems: alcohol gel (A), hydrogel (H) and micellar gel (M).

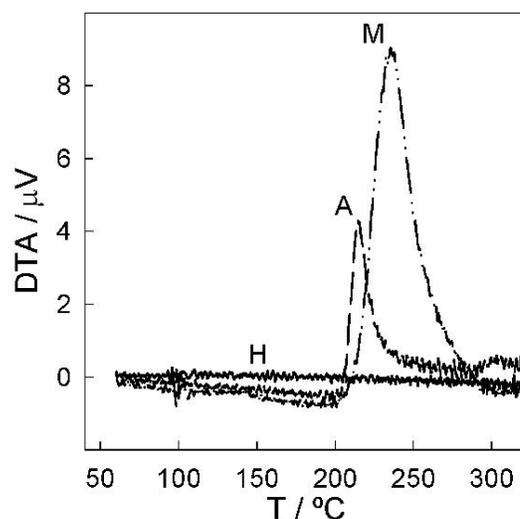


Figure 5. DTA response in different aged TiO<sub>2</sub> gels: alcoholgel (A), hydrogel (H) and micellar gel (M).

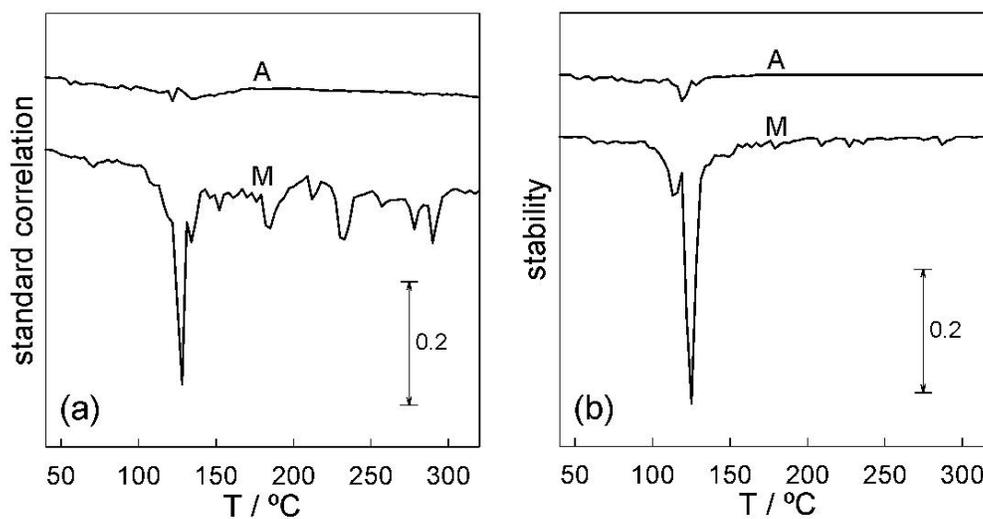


Figure 6. Standard correlation (a) and stability analysis (b) of photoacoustic signals as a function of temperature for different aged TiO<sub>2</sub> gels systems: alcoholgel (A), hydrogel (H) and micellar gel (M).

## 5. CONCLUSIONS

In this work we demonstrate that correlation analysis of photoacoustic waves obtained upon excitation by a laser pulses allow to obtain valuable phenomenological information on the stability of systems evolving from sols to aged gels. This analysis provides a powerful tool for understanding complex systems requiring more information than that

obtained by the conventional analysis considering only the first wave of the photoacoustic signal.

Two main conclusions can be drawn from the PA results obtained for titania based sols.

(I) The evolution before and after gelation has an oscillatory behaviour either at constant temperature or under heating. Although below  $t_g$  the oscillations can be due to simultaneous evaporation of the solvent and gelation, for alcogel and hydrogel it is possible to discriminate  $t_g$  from the stability plots. On the other hand, the oscillations above  $t_g$  are more evident for the most particulated systems, and are negligible for long term aged gels.

(II) At least for titania gels, there is a distinguishable transition in the 100–150°C range without latent heat evolution that probably corresponds to a specific molecular rearrangement.

Future work with other gel systems is envisaged in order to determine the chemistry involved in the processes leading to both oscillations and transitions.

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